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**CATION ORDERING IN ORTHOPYROXENES AND COOLING RATES OF METEORITES:
LOW TEMPERATURE COOLING RATES OF ESTHERVILLE, BONDOK AND SHAW : J.**

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The cooling rates of meteorites provide important constraints on the size of their parent bodies, and their accretionary and evolutionary histories. However, the cooling rates obtained so far from the commonly used metallographic, radiometric and fission-track methods have been sometimes quite controversial, such as in the case of the mesosiderites and the meteorite Shaw. The metallographic method suggests extremely slow cooling rate for the mesosiderites, $\leq 1^\circ\text{C}/\text{Ma}$, which seems difficult to reconcile with the brecciated nature of the silicates in these rocks, suggesting exposure to near-surface environments [1]. For Shaw, which is an L-group chondrite consisting of three intermingled lithologies, the metallographic method suggests a relatively rapid cooling rate, $\sim 3^\circ\text{C}/10^3$ years at $450\text{--}550^\circ\text{C}$, wherever metal occurs in this meteorite [2], which is in contrast to the very slow cooling rate, $1^\circ\text{C}/\text{Ma}$ at $T \leq 350^\circ\text{C}$, deduced by the fission track method [3]. We have undertaken a systematic study of the cooling rates of meteorite using a different approach, which involves single crystal x-ray determination of Fe^{2+} -Mg ordering in orthopyroxenes (OPx) in meteorites, subject to bulk compositional constraints, and numerical simulation of the evolution of the ordering state as a function of cooling rate, within the framework of the thermodynamic and kinetic principles governing cation ordering [4]. In this work, we report the results obtained for OPx crystals from Shaw and two mesosiderites, Estherville and Bondok.

Five crystals, which appeared well suited for single crystal x-ray study, were used for site occupancy refinement. These crystals did not show any exsolution either in back scattered electron imaging in a scanning electron microprobe or in single crystal x-ray precession photographs. Owing to the sensitivity of cooling rate calculations to site occupancy determinations, especially at low Fe content [5], we have carried out extremely high precision x-ray and microprobe analyses of the crystals, as briefly described below.

Each crystal was ground to nearly spherical shape to facilitate absorption correction, and x-ray intensities of a large number ($\sim 2000 - 2800$) of non-equivalent reflections from each crystal were determined on an automated single crystal x-ray diffractometer (MoK α rad, 50 kv, 20 mA, scan speed $1.5^\circ/\text{min}$). Each non-equivalent reflection represents an average of the equivalent (hkl) and ($\bar{h}\bar{k}l$) pair. After collection of the x-ray data, all crystals were analyzed in a JEOL electron microprobe, and found to be homogeneous within the precision of probe analysis. The standards consisted of synthetic end-member pyroxenes and garnets. The bulk composition of each crystal was first determined by averaging over 16 spot analyses and then refined by adjusting the concentration of the elements within one standard deviation of the average to meet the following crystal-chemical constraints for six oxygen per formula unit: (a) the total positive charge = 12.000, (b) the total occupancy of T(tetrahedral)-sites = the total occupancy of the M(octahedral)-sites = 2.000, and (c) the difference between the charge deficiency in the T-site (due to substitution for Si) and the charge excess in the M-site (due to substitutions for $2+$ ions) = 0.000. The composition of each spot was determined by counting for 100 s at 15 kV accelerating voltage and 25 nA beam current.

The site occupancies of each crystal were refined using the proprietary program RFINE 90, which is an updated version of RFINE4 [6]. It was assumed that all Cr, Ti and Al(VI) were confined to M1 site, Ca and Na were restricted to M2 site, whereas Fe^{2+} and Mn^{2+} fractionated similarly between the two octahedral sites, M1 and M2. The closure temperature (T_c) of the observed ordering state of each crystal (which decreases with decreasing cooling rate) was determined by comparing the intracrystalline Fe(+Mn)-Mg distribution coefficient (K_d) with the

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recent calibration of the variation of $\ln K_d$ vs $1/T$ of an OPx crystal from Johnstown meteorite of similar composition [7], as recently revised by Molin and Ganguly ($\ln K_d = -2914/T + 0.801$), following the above procedure of site occupancy refinement. The results are as follows ($\text{Fe}^* = \text{Fe}^{2+} + \text{Mn}^{2+}$; uncertainty: $\pm 1 \sigma$).

Meteorite	Bondoc		Estherville		Shaw
Crystal No.	1	2	1	2	4
M1 Site:					
Mg	.9791(17)	.9755(20)	.9730(19)	.9724(14)	.9801(16)
Fe*	.0019	.0025	.0060	.0056	.0049
Al	.002	.002	.003	.003	.000
Cr ³⁺	.016	.019	.016	.017	.015
Ti ⁴⁺	.001	.001	.002	.002	.000
M2 Site:					
Mg	.6495	.6415	.6491	.6516	.6384
Fe*	.3295	.3365	.3249	.3224	.3316
Ca	.020	.022	.026	.026	.027
Na	.001	.000	.000	.000	.003
Rw	.021	.023	.022	.018	.019
T _c (°C)	185	203	288	282	262

Cooling rates were calculated from the above site occupancy data, according to the method developed by Ganguly(4), using the available data on Fe-Mg order-disorder kinetics in orthopyroxene as a function of temperature and composition [8], and assuming an asymptotic cooling law, $1/T = 1/T^0 + \eta t$, where T^0 is the initial temperature and η is a cooling time constant ($\text{K}^{-1}\text{yr}^{-1}$). The calculated cooling rates ($dT/dt = -\eta T^2$) are strictly valid near T_c , and are fairly insensitive to errors in the estimation of T^0 .

The results suggest that at 250°C, the **Bondoc** meteorite had cooled at ≤ 1 K/Ma, whereas **Estherville** had cooled at ~ 8 K/Ma. Although the uncertainty of the site occupancy data of the OPx crystals from Estherville permit a cooling rate of ≤ 1 K/Ma, it seems likely that it had cooled somewhat faster than Bondoc since both crystals from Estherville yield essentially the same cooling rate. The ordering state of **Shaw** yields a cooling rate of ≤ 0.3 K/Ma at 250°C and ≤ 4 K/Ma at 350°C; if the site occupancies are recalculated assuming that 50% of Cr is in the 2+ state, the cooling rate increases by a factor of 10. Thus, our result supports the slow cooling rate for Shaw obtained from the fission track method. Further work on Shaw is in progress to determine if it has silicate domains characterized by significantly faster cooling rate of OPx, similar to that deduced from metallographic methods in metal-bearing domains.

- [1] Bogard D. et al. (1990) *GCA*, 54, 2549; [2] Taylor G.J. et al. (1979) *GCA*, 43, 323; [3] Pellas P. et al. *LPSC IX*, 879. [4] Ganguly J. (1982), *In Saxena S. K. (ed) Adv Phys Geochem*, 2, 58. [5] Ganguly J. et al. (1989) *LPSC XX*, 331. [6] Finger, L.W. and Prince, E. (1975) *NBS Tech Note 854*; [7] Molin G. et al. (1991) *EPSL*, 105, 261. [8] Besancon JR (1981) *Amer. Min.*, 66, 965.